

Claims

1. A compound of the formula $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$ where R is a $\text{C}_1\text{-C}_5$ alkyl, R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl, Li, Na, H, and K, and M is selected from the group consisting of
5 H, Li, K, Na, $\text{R}'_3\text{NH}^+$, or mixtures thereof, where R' is a $\text{C}_1\text{-C}_5$ alkyl.
2. A compound of the formula $\text{ROC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$ where R is a $\text{C}_1\text{-C}_5$ alkyl and R^1 is selected from the group consisting of Li, H, K and Na, and R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl.
- 10 3. A sulfonimide bearing compound of the formula $\text{HOC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$ where R^1 is selected from the group consisting of Li, K, H, and Na, and R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl.. comprising,
reacting $\text{ROC}_6\text{H}_4\text{SO}_2\text{Cl}$ where R is a $\text{C}_1\text{-C}_5$ alkyl with $\text{R}_f\text{SO}_2\text{NH}_2$ where R_f is any $\text{C}_1\text{-C}_8$ perfluoroalkyl, and a base selected from the group consisting of Trimethylamine,
15 Triethylamine, Pyridine, Imidazole, Pyrimidine or mixtures thereof in the presence of a first solvent selected from the group consisting of Acetone, Acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, Dimethyl sulfoxide, Hexamethylphosphoramide, Nitromethane, Pyridine, Tetrahydrofuran or mixtures thereof to produce a first intermediate compound of the formula $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$
20 where M is $\text{R}'_3\text{NH}^+$, where R' is a $\text{C}_1\text{-C}_5$ alkyl,
reacting the first intermediate compound with an alkali metal salt selected from the group consisting of Lithium methoxide, Lithium ethoxide, Lithium tert-butoxide, Lithium phenolate, Lithium hydroxide, Sodium methoxide, Sodium ethoxide, Sodium tert-butoxide, Sodium phenolate, Sodium hydroxide Potassium methoxide, Potassium
25 ethoxide, Potassium phenolate, Potassium tert-butoxide, Potassium hydroxide or mixtures thereof in the presence of a second solvent selected from the group consisting of Methanol, Ethanol, Isopropanol, tert-Butanol, Acetone, Acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, Dimethyl sulfoxide,

Hexamethylphosphoramide, Nitromethane, Tetrahydrofuran or mixtures thereof to produce a second intermediate of the formula $\text{ROC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$ where M is selected from the group consisting of Li, Na and K, R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl, and R is a $\text{C}_1\text{-C}_5$ alkyl,

5 reacting the second intermediate with an alkali alkane thiolate selected from the group consisting of sodium ethane thiolate, lithium ethane thiolate, potassium ethane thiolate and mixtures thereof to produce a sulfonimide bearing compound of the formula $\text{HOC}_6\text{H}_4\text{SO}_2\text{NMSO}_2\text{R}_f$, where M is selected from the group consisting of Li, Na, H and K, and R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl.

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4. An alkali sulfonimide bearing compound of the formula $\text{ROC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$ where R and R^1 are the same or different and each of R and R^1 are selected from the group consisting of Li, Na, H, and K, and R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl.

15 5. The alkali sulfonimide bearing compound of claim 4 wherein R and R^1 each are Na.

6. An amine terminated sulfonimide bearing compound of the formula $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f$ where R^1 is selected from the group consisting of Li, Na, H, and K, and R_f is a $\text{C}_1\text{-C}_8$ perfluoroalkyl.

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7. The amine terminated sulfonimide bearing compound of claim 7 where R^1 is Na.

8. A method of making an alkali phenoxy sulfonimide functionalized polyphosphazene comprising,

25 reacting a polyphosphazene of the formula $(\text{N}(\text{PCl}_2)_n$, where $n \geq 3$ with an alkali oxide derivative selected from the group consisting of sodium p-methyl phenoxide, lithium p-methyl phenoxide, potassium p-methyl phenoxide to produce a first intermediate of the formula $[(\text{NP}(\text{Cl})_x(\text{OC}_6\text{H}_4)_{2-x})_n]$, where $n \geq 3$,

reacting the first intermediate with a second alkali salt $R^1OC_6H_4SO_2NR^1SO_2R_f$, where R^1 is Li, K, or Na, and where R_f is a C_1 - C_8 perfluoroalkyl, to produce a second intermediate of the formula such as

$[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_y(Cl)_{2-x-y}]_n$, where R^1 is Li, Na, or K, and where R_f is a C_1 - C_8 perfluoroalkyl.

reacting the second intermediate with a third alkali salt selected from the group consisting of $H_3CC_6H_4ONa$, $NaOC_6H_5$, $NaOC_6H_4CF_3$, $LiOC_6H_4CH_3$, $LiOC_6H_5$, $LiOC_6H_4CF_3$, $H_3CC_6H_4OK$, KOC_6H_5 and $KOC_6H_4CF_3$ to produce an alkali phenoxy sulfonimide functionalized polyphosphazene of the formula such as

$[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_{2-x}]_n$, where R_f is a C_1 - C_8 perfluoroalkyl, and where R^1 is Li, K or Na.

10. The method of claim 9 wherein R^1 is Na.

11. A method of making a phenoxy sulfonimide functionalized polyphosphazene comprising,

reacting polyphosphazene of the formula $(NPCl_2)_n$, where $n \geq 3$ with $R^1OC_6H_4CH_3$ and $R^1OC_6H_4SO_2NR^1SO_2R_f$ where R^1 is selected from the group consisting of Na, K and Li and R_f is a C_1 - C_8 perfluoroalkyl, to produce a reaction product, and reacting the reaction product with $R^1OC_6H_4CH_3$ where R^1 is selected from the group consisting of Na, K, H and Li to produce an alkali phenoxy sulfonimide functionalized polyphosphazene of the formula $[NP(OC_6H_4SO_2NR^1SO_2R_f)_x(OC_6H_4CH_3)_{2-x}]_n$.

12. The method of claim 11 wherein R^1 is Na.

13. A sulfonimide functionalized polyphosphazene homopolymer of the formula $[NP(OC_6H_4SO_2NR^2SO_2R_f)_2]_n$ where R^1 is selected from the group consisting of Li, Na, H and K.

14. The homopolymer of claim 13 wherein R¹ is Na.

15. A method of manufacture of a sulfonimide functionalized polyphosphazene homopolymer of the formula $[NP(OC_6H_4SO_2NR^1SO_2R_f)_2]_n$ where R¹ is selected from the group consisting of Li, Na, H, and K and , R_f is a C₁-C₈ perfluoroalkyl, comprising, reacting (NPCL₂)_n, where n ≥ 3 with R¹OC₆H₄NR¹SO₂R_f where R¹ is selected from the group consisting of Li, K and Na and , R_f is a C₁-C₈ perfluoroalkyl, at a temperature of about 60 °C to about 200 °C at a pressure of about ambient to about 12 bar for about 12 hours to about 40 hours.

16. The method of claim 15 wherein R¹ is Na.

17. A phenoxy sulfonimide functionalized polyphosphazene copolymer of the formula $[NP(ZR^2)_x(ZC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$, where , R_f is a C₁-C₈ perfluoroalkyl, where R² is selected from the group consisting of -CH₂CH₃, -C₆H₄CH₃, -CH₂CH₂OCH₂CH₂OCH₃, -CH₂CH₂OTHP, -C₆H₄COOPr, -CH₂CF₃, -CH₂CF₂OCF₂CF₂OCF₃, -C₆H₄CF₃, -C₆F₅, and mixtures thereof, Z is O or NH, and R¹ is selected from the group consisting of Na, Li, H, and K.

18. The copolymer of claim 17 wherein R² is -C₆H₄CH₃, and Z is -O-.

19. The copolymer of claim 17 wherein R¹ is Na.

20. A method of making a phenoxy sulfonimide functionalized polyphosphazene copolymer of the formula $[NP(ZR^2)_x(ZC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$, where , R_f is a C₁-C₈ perfluoroalkyl, where R² is selected from the group consisting of -CH₂CH₃, -C₆H₄CH₃, -CH₂CH₂OCH₂CH₂OCH₃, -CH₂CH₂OTHP where THP is tetrahydropyranl, -C₆H₄COOPr, -CH₂CF₃, -CH₂CF₂OCF₂CF₂OCF₃, -C₆H₄CF₃, -C₆F₅, Z is O or NH, and R¹ is

selected from the group consisting of Na, Li and K, comprising,

reacting $(\text{PNCl}_2)_n$, where $n \geq 3$ with a first amount of compound of the formula R^3R^2 where R^3 is selected from the group consisting of $-\text{NaO}$, $-\text{LiO}$, $-\text{KO}$, NH_2 or mixtures thereof, R^2 is selected from the group consisting of $-\text{CH}_2\text{CH}_3$, $-\text{C}_6\text{H}_4\text{CH}_3$,
5 $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{CH}_2\text{OTHP}$ where THP is tetrahydropyranyl, $-\text{C}_6\text{H}_4\text{COOPr}$, $-\text{CH}_2\text{CF}_3$, $-\text{CH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$, $-\text{C}_6\text{H}_4\text{CF}_3$, $-\text{C}_6\text{F}_5$, or mixtures thereof, with a second amount of a compound of the formula $\text{R}^2\text{C}_6\text{H}_4\text{SO}_2\text{NHSO}_2\text{R}_f$ where R_f is a C_1 - C_8 perfluoroalkyl, where R^2 is selected from the group consisting of $-\text{NaO}$, $-\text{LiO}$, $-\text{KO}$, NH or mixtures thereof, at a first temperature of about 60°C to about 200°C to
10 produce a reaction product,

reacting the reaction product with R^3R^2 at a second temperature of 60°C to about 200°C at a pressure of about 3.5-4 bar.

21. A haloalkoxy sulfonimide functionalized polyphosphazene of the formula

15 $(\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_2)_x (\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{(1-x)}$ where R^1 is selected from the group consisting of Na, Li, H, and K, and where R_f is a C_1 - C_8 perfluoroalkyl.

22. The haloalkoxy sulfonimide functionalized polyphosphazene of claim 21 where R^1 is Na.

23. A method of manufacture of haloalkoxy sulfonimide functionalized polyphosphazene of the formula

$[\text{NP}(\text{OCH}_2(\text{CF}_2)_4\text{H})_x (\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{2-x}]_n$ where R^1 is selected from the group consisting of Na, Li and K and , R_f is a C_1 - C_8 perfluoroalkyl, comprising,

25 reacting $(\text{NPCl}_2)_n$, where $n \geq 3$ with an alkali fluoroalkoxide selected from the group consisting of $\text{NaOCH}_2(\text{CF}_2)_4\text{H}$, $\text{NaOCH}_2\text{CF}_3$, $\text{NaOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$, $\text{LiOCH}_2(\text{CF}_2)_4\text{H}$, $\text{LiOCH}_2\text{CF}_3$, $\text{LiOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$, $\text{KOCH}_2(\text{CF}_2)_4\text{H}$, KOCH_2CF_3 , and $\text{KOCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$ to displace about 50% of the Cl in the $(\text{PNCl}_2)_n$, where

n≥3 to form a first reaction product,

reacting the first reaction product with an alkali phenoxy sulfonimide of the formula $R^1OC_6H_4SO_2NMSO_2R_f$ where R^1 is selected from the group consisting of Na, Li and K to produce a second reaction product,

5 reacting the second reaction product with an excess of an alkali fluoroalkoxide selected from the group consisting of $NaOCH_2(CF_2)_4H$, $NaOCH_2CF_3$, $NaOCH_2CF_2OCF_2CF_2OCF_3$, $LiOCH_2(CF_2)_4H$, $LiOCH_2CF_3$, $LiOCH_2CF_2OCF_2CF_2OCF_3$, $KOCH_2(CF_2)_4H$, $KOCH_2CF_3$, and $KOCH_2CF_2OCF_2CF_2OCF_3$ to produce a haloalkoxy sulfonimide functionalized polyphosphazene of the formula

10 $[NP(OCH_2(CF_2)_4H)_2]_x(OC_6H_4SO_2NR^1SO_2R_f)_{2-x}]_n$ where R^1 is selected from the group consisting of Na, Li and K and R_f is a C_1 - C_8 Perfluoroalkyl,.

24. A blend of sulfonimide functionalized polyphosphazene comprising a sulfonimide functionalized polyphosphazene and another polymer selected from the group

15 consisting polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PDVF), polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), polystyrene (PS), polybutadiene (BR), polyvinylidene chloride (VDC), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVAL), polyvinyl acetate (PVA), polyphenylene oxide (PPO), polyether ether ketone (PEEK), polyethylene terephthalate (PET), polybutylene
20 terephthalate (PBT), polycarbonate (PC), polyether sulfone, polybenzimidazoles (PBI), polydimethyl siloxane, polyphenylene sulfide (PS), polypyrrole, polyphenylene, polyaniline, poly(bis(pentoxy)phosphazene), poly(bis(phenoxy)phosphazene), poly((methoxyethoxyethoxy)(m-methyl phenoxy)phosphazene), styrene-acrylonitrile copolymers (SAN), Acrylonitrile-butadiene-styrene terpolymers (ABS) and ethylene-
25 methacrylic acid copolymer.

25. A blend of claim 23 where the non-phosphazene polymer is polyvinylidene fluoride.

26. A composition comprising a sulfonamide functionalized polyphosphazene polymer and an additive selected from the group consisting of examples such as additives such as carbon black, graphite, platinum, ruthenium, silica, montmorillonite, clay, titanium dioxide, zirconium oxide, phosphoric acid, phosphotungstic acid, silicomolybdic acid, phosphomolybdic acid, salts such as $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{CF}_3$, hexaphenoxycyclotriphosphazene, di(m-methylphenoxy)tetra(trifluoroethoxy)cyclotriphosphazene, plasticizers such as methanol, ethanol and hexane, cross-linkers such as diamines.
27. A membrane comprising a sulfonimide functionalized polyphosphazene of the formula $[\text{NP}(\text{OC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_x(\text{OC}_6\text{H}_4\text{CH}_3)_{2-x}]_n$, where R^1 is Li, Na, K, or H and R_f is a C_1 - C_8 perfluoroalkyl.
28. A membrane comprising a sulfonamide functionalized polyphosphazene of the formula $[\text{NP}(\text{ZR}^2)_x(\text{ZC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_3)_{2-x}]_n$, where R^1 is Li, Na, K, or H, Z is O or NH, and R^2 is an alkyl, aryl, fluorinated alkyl, perfluorinated alkyl, fluorinated aryl, functionalized alkyl or functionalized aryl and R_f is a C_1 - C_8 perfluoroalkyl.
29. The membrane of claim 26 wherein the polyphosphazene is cross linked.
30. The membrane of claim 27 wherein the polyphosphazene is cross linked.
31. The membrane of claim 28 wherein the polyphosphazene is cross linked.
32. A fuel cell comprising a membrane of a polyphosphazene of the formula $[\text{NP}(\text{ZR}^2)_x(\text{ZC}_6\text{H}_4\text{SO}_2\text{NR}^1\text{SO}_2\text{R}_f)_{2-x}]_n$, where R^1 is Li, Na, K, or H, Z is O or NH, and R^2 is an alkyl, aryl, fluorinated alkyl, perfluorinated alkyl, fluorinated aryl, functionalized alkyl or functionalized aryl, R_f is a C_1 - C_8 perfluoroalkyl, and where the

polyphosphazene is cross linked or uncross-linked.

33. A fuel cell comprising a membrane of a polyphosphazene of the formula
[NP(OC₆H₄SO₂NR¹SO₂R_f)_x(OC₆H₄CH₃)_{2-x}]_n, where R_f is a C₁-C₈ perfluoroalkyl, where
5 the polyphosphazene is cross linked.

34. A method of making a lithiated phenoxy sulfonimide functionalized
polyphosphazene [NP(OR⁵)_x(OC₆H₄SO₂NLiSO₂R_f)_{2-x}]_n where R_f is a C₁-C₈
perfluoroalkyl and where R⁵ is an oligo-oxy substituent selected from the group
10 consisting of -CH₂CH₂OCH₂CH₂OCH₃, -CH₂CF₂OCF₂CF₂OCF₃, -
CH₂CH₂OCH₂CH₂OCH₂CH₂OCH₃ comprising,

forming an aqueous, acidic solution of [NP(OR⁵)_x(OC₆H₄SO₂NHSO₂R_f)_{2-x}]_n and
subjecting the solution to dialysis against a LiCl solution.

15 35. The method of making the copolymer in claim 34 where R⁵ is
-OCH₂CH₂OCH₂CH₂OCH₃ and the polyphosphazene has the formula
[NP(OCH₂CH₂OCH₂CH₂OCH₃)_x(OC₆H₄SO₂NLiSO₂R_f)_{2-x}]_n where R_f is a C₁-C₈
perfluoroalkyl.